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Evidence for the facile formation of nitrogen-containing compounds from NO_x and propene species on tungstated zirconia-based catalysts: Are these compounds active or spectator species in the selective catalytic reduction of NO_x by C_3H_6?

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ABSTRACT

The propene selective catalytic reduction (C_3H_6-SCR) of NO_x is investigated on WO_x–ZrO_2 and Pd/WO_x–ZrO_2. Temperature-programmed surface reaction (TPSR) experiments provide evidence of the decomposition of organic nitrogen-containing species formed through the interaction of C_3H_6 and ad-NO$_x$, for which a C/N ratio of 3 is estimated. The TPSR of preadsorbed NO_x in C_3H_6–O_2–He also suggests the presence of two R–NO$_x$ species, C_3H_5–O–NO (propenyl nitrite) and C_3H_5–NO_2 (nitropropene), decomposing in distinct temperature regions. The addition of Pd to WO_x-ZrO_2 promotes the decomposition of nitropropene, whereas that of propenyl nitrite is scarcely affected. It is also suggested that R–NO$_x$ are not active intermediates in C_3H_6-SCR on Pd/WZ catalysts but are more likely spectators. The activity for C_3H_6-SCR is attributed to Pd^0 species, formed by in situ reduction of oxidized Pd species by C_3H_6, via the well-established decomposition mechanism. In light of the new findings about the formation–decomposition of R–NO$_x$, results reported previously on a Pd/$Ce_{0.68}Zr_{0.32}O_2$ catalyst [C. Thomas, O. Gorce, C. Fontaine, J.-M. Krafft, F. Villain, G. Djéga-Mariadassou, Appl. Catal. B Environ. 63 (2006) 201], for which metal–support interactions prevent PdO_x reduction and C_3H_6-SCR reaction mechanism is different from that on Pd^0 sites, are widened.

1. Introduction

Although tungstated-zirconias (WO_x–ZrO_2) showed interesting catalytic properties in the skeletal isomerization of butane or pentane more than twenty years ago [1], their use as catalyst, or catalyst support, has been limited till the late nineties. Due to the strong Brønsted acidity of these materials [1–12], they have been used mainly for the isomerization of short-chain alkanes [2,6,13–24]. The redox character of W has also been demonstrated in the presence of H_2 and/or hydrocarbons [10,25]. It has been suggested that this redox character is the source of "temporary" Brønsted acidity which compensates for the negative charge of the polyoxotungstate domains [3–5,11,26,27].

Apart from the isomerization reactions for which the bifunctional character of the noble metal-promoted WO_x–ZrO_2 catalysts is well-suited, very few studies have been reported on the use of WO_x–ZrO_2-supported materials in the selective reduction of NO_x by hydrocarbons (HC-SCR) [28–32]. To our knowledge, palladium-promoted WO_x–ZrO_2 catalysts have been studied mainly for CH_4-SCR [28–32]. In their pioneering work, Resasco and coworkers also studied the influence of the reductant on the HC-SCR performances of Pd/WO_x–ZrO_2 catalysts [29]. These authors showed that important differences due to the nature of the reducing agent exist. The addition of W promotes CH_4-SCR, whereas it inhibits C_3H_6-SCR. In addition, the selectivity toward N_2 decreases when using C_3H_6 instead of CH_4. For a Pd/WO_x–ZrO_2 catalyst with 13.2 wt% W, it must be emphasized, however, that NO conversion in C_3H_6-SCR (approaching 90% at 435 °C) is about twice that found in CH_4-SCR under their experimental conditions.

On the basis of FTIR measurements, Weingand et al. have reported recently on the formation of an organic deposit through the interaction of nitrates and propene on WO_x–ZrO_2 [33]. These authors claim that the formed nitrogen-containing molecules, also reported as R–NO$_x$ species in the literature, decompose to isocyanates which then react with $NO + O_2$ to yield N_2. The involvement of the formed R–NO$_x$ species as intermediates of the HC-SCR has been reported in many studies [34–36]. Overall, this conclusion was reached based on the FTIR signature of R–NO$_x$ compounds formed with a wide variety of hydrocarbons such as CH_4 [37–39], C_2H_5OH [40,41], C_3H_6 [42–56], C_3H_8 [45,53,57,58], C_4H_{10} [57] or $C_{10}H_{22}$ [59] on zeolite- and oxide-supported catalysts. Although

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FTIR is a powerful technique to investigate the nature of the compounds formed on the catalyst surface, this technique (i) does not always provide detailed and reliable information on the thermal stability of the formed organic nitrogen-containing species and (ii) is inappropriate to determine their carbon to nitrogen stoichiometry.

This work aims at providing further insights on the facile formation and the decomposition of R–NO_x compounds on WO_x–ZrO_2-supported catalysts. By means of a reactivity approach, their thermal stability is ascertained and their carbon to nitrogen stoichiometry is estimated. On the Pd/WO_x–ZrO_2 catalyst, the results indicate that the organic nitrogen-containing compounds are more likely spectators in the C_3H_6-SCR reaction rather than intermediates. The role of Pd in R–NO_x decomposition is discussed and a comparison is provided with results published previously on $Ce_{0.68}Zr_{0.32}O_2$-supported samples [60].

2. Experimental

2.1. Catalyst synthesis

The tungstated zirconia (WO_x–ZrO_2: WZ) support was synthesized by suspending 3 g of commercial zirconium oxyhydroxide ($ZrO_x(OH)_{4-2x}$, XZO880/01), provided by MEL Chemicals (Manchester, UK), in 30 ml of an aqueous solution of ammonium metatungstate (0.49 g of $(NH_4)_6[W_{12}O_{40}H_2]$, Fluka). The suspension was stirred vigorously for 1 h at RT before being heated up to 110 °C for 20 h under reflux. Water was then gently evaporated and the material was dried in air at 110 °C for 18 h before being calcined up to 650 °C, with a heating rate of 5 °C min^{-1}, for 3 h under flowing air (33 mL min^{-1} g_{cat}^{-1}).

Two batches of tungstated zirconia-supported Pd catalysts (0.2 wt% Pd), namely Pd/WZ1 and Pd/WZ2, were prepared according to a method similar to that described for WZ. For the supported Pd catalysts, $Pd(NO_3)_2 \cdot 3H_2O$ (Johnson Matthey) was introduced to the zirconium oxyhydroxide/ammonium metatungstate suspension.

2.2. Catalyst characterization

The metal contents were determined by chemical analyses (CNRS—Vernaison). The specific surface areas were determined by physisorption of N_2 at 77 K using a Quantasorb Jr. dynamic system equipped with a thermal conductivity detector (TCD). The specific surface areas were calculated using the BET method. X-ray diffraction (XRD) patterns of WZ, Pd/WZ1 and Pd/WZ2 were collected on a Siemens D500 diffractometer with a CuK_α monochromatized radiation in 2θ from 12 to 70° with a scanning rate of 0.013° s^{-1}. Identification of the crystalline phases was made with the help of the Joint Committee Powder Diffraction Standard (JCPDS) files.

2.3. Catalytic runs

Prior to catalytic runs, the samples (0.5 g) were calcined in situ in O_2(20%)/He at 500 °C or 600 °C (3 °C min^{-1}) for 2 h with a flow rate of 100 mL_{NTP} min^{-1} (gas hour space velocity (GHSV) of about 17,000 h^{-1}), unless otherwise specified.

The experiments were carried out in a U-type quartz reactor (15 mm i.d.). The samples were held on plugs of quartz wool, and the temperature was controlled by a Eurotherm 2408 temperature controller using a K type thermocouple. Reactant gases were fed from independent mass flow controllers (Brooks 5850TR). The total flow was 230 mL_{NTP} min^{-1} which corresponds to a GHSV of about 40,000 h^{-1}.

Typically, the composition of the C_3H_6–NO–O_2 reaction mixture was: 480 ppm C_3H_6, 400 ppm NO and 7% O_2 in He. The reactants, diluted in He, were used as received and were fed from independent gas cylinders (Air Liquide).

The reactor outflow was continuously monitored using a combination of four detectors. A chemiluminescence NO_x analyzer (Thermo Environmental Instruments 42C-HT) allowed the simultaneous detection of both NO and NO_2. An Ultramat 6 IR analyzer was used to monitor N_2O. CO and CO_2 were analyzed using an infrared detector (Maihak 710). A FID detector (Thermo Environmental Instruments 51C-LT) was used to determine the concentration of hydrocarbons (HC). The response time of the detectors, including time lags due to gas transport in the lines from the outlet of the reactor to the detectors, were 0.25, 0.42 and 0.67 min for CO–CO_2–N_2O, NO–NO_2 and HC, respectively. Given that the transient experiments were carried out at a heating rate of 3 °C min^{-1}, these response times resulted in negligible temperature offsets of 0.8, 1.3 and 2.0 °C, respectively. Although it can be seen that the various traces were recorded within almost 1 °C difference only, the traces shown in this work were corrected from these very small differences in response time. We also checked that, under our experimental conditions, C_3H_6, CO and CO_2 had a negligible response on the N_2O IR analyzer. The conversion of NO_x was calculated as follows:

$$\text{Conversion of } NO_x\ (\%) = \frac{[NO_x]_{\text{inlet}} - [NO_x]_{\text{outlet}}}{[NO_x]_{\text{inlet}}},$$

where $[NO_x]_{\text{inlet}}$ and $[NO_x]_{\text{outlet}}$ are the concentrations of NO_x at the inlet and at the outlet of the reactor, respectively.

After exposure to the appropriate gas mixture at RT, temperature transient experiments were carried out from RT to 600 °C at a heating rate of 3 °C min^{-1}. Before the transient experiments, the catalyst samples were flushed in He at RT to remove weakly chemisorbed species. Various transient experiments were performed including (i) temperature-programmed surface reactions (TPSR) in O_2–He or C_3H_6–O_2–He, and (ii) temperature-programmed oxidations (TPO) in C_3H_6–O_2–He.

3. Results

3.1. Structural characterization of the catalysts

The composition of the catalysts and their specific surface areas are listed in Table 1. The amount of W in the synthesized materials is close to 13 wt%. The specific surface areas of the Pd/WZ samples is about 85 $m^2\,g^{-1}$, whereas that of WZ is slightly lower (68 $m^2\,g^{-1}$). This translates to tungsten surface densities of 6.8 and 4.8 W atoms nm^{-2} for the WZ and Pd/WZ samples, respectively.

The tetragonal ZrO_2 (t-ZrO_2) crystalline phase predominates for all samples, as indicated by the presence of diffraction peaks at 30.2, 35.3, 50.4, 60.3 and 62.9° (JCPDS file 50-1089) as shown in Fig. 1. This observation agrees with previous reports stating that the transformation of the t-ZrO_2 phase to the thermodynamically more stable monoclinic ZrO_2 phase (m-ZrO_2) can be delayed by the addition of transition metals [61,62]. The reflections of weak intensity observed at 28.3 and 31.5° are attributed to the presence of small amounts of m-ZrO_2 (JCPDS file 37-1484), the latter reflection being seen as a shoulder of the intense diffraction peak of the (111) plane of t-ZrO_2 at 30.2°. Detailed analysis of the 23–25° region clearly shows the presence of crystalline WO_3 (JCPDS file 32-1395) on the Pd-free WZ sample, with diffraction peaks at 23.1, 23.7 and

Table 1

Chemical elemental analyses and specific surface areas of the synthesized catalysts calcined at 650 °C for 3 h

Catalyst	W (wt%)	Pd (wt%)	Specific surface area ($m^2\,g^{-1}$)	δ (W at. nm^{-2})
WZ	14.2	–	68	6.8
Pd/WZ1	12.8	0.20	89	4.7
Pd/WZ2	11.9	0.19	80	4.9